

Fabrication of Gas Filter to Remove Toxic Gas Using Layer-by-layer Adsorption Technique

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Recent investigations have shown that layer-by-layer adsorption technique is useful as material separation in composite membranes, e.g. for the separation of gases, ultra- and hyper filtration, liquid permeation and pervaporation. In this study we report the fabrication of new composite membranes for removing toxic gas as an application of the alternate deposition technique. The fabrication process of the heterostructure using polyelectrolyte, low molecular weight organic compounds and metal oxide was studied. Adsorbed amount of films was characterized with quartz crystal microbalance (QCM). As the results, it was found that the different heterostructure was fabricated by simply changing conditions such as drying and stirring process, the pH value of the solutions and dielectric constant of dissolvent. Gas removal measurements have been carried out for basic gases (trimethylamine), sulfur gases (mercaptan) and aldehydes. The advantage of the alternate deposition technique is that it is very effective for the fabrication of heterostructure and it can fabricate thin film on a complicated substrate such as a honeycomb structure. It was also found that the gas removal performance was improved by using the alternately deposition method.

Key words: self-assembly, layer-by-layer adsorption, gas adsorption, small molecule, metal oxide

1. INTRODUCTION

Layer-by-layer self-assembly technique is based on electrostatic interactions between cationic and anionic materials and has been widely used in building up the thin film whose architecture and thickness can be controlled with the molecular level. By analyzing the physics involved in the adsorption mechanism, it's confirmed that electrostatic interactions, hydrogen bond and hydrophobic effect, charge-transfer complexes or covalent bonds play a crucial role in the adsorption mechanism of layer-by-layer self-assembly film [1-5]. Since these may be the driving force for adsorption, it is one of the advantages of this technique that it enables to assemble various charged materials.

Recent investigations have shown that this technique might also be useful as separation layers in composite membranes, e.g. for the separation of gases, ultra- and hyper filtration, liquid permeation and pervaporation [6-9]. In this study we report on fabrication of new organic/inorganic membranes for removing toxic gas as an application of layer-by-layer self-assembly technique. As the advantage using alternate assembly technique, it isn't required a large apparatus firstly. Also it has an effect to a mixed gas by

fabricating hetero structure using much kind of materials and it can be fabricated films on a complicated plate such as a honeycomb structure.

2. EXPERIMENT

2.1 Materials

Because primary amines are reactive nucleophiles and readily attack carbonyl carbon atoms of aldehydes and ketones, primary amine compounds were used to adsorb aldehyde compounds one of the toxic gases. Primary amine compounds used were hydroxylamine (HA) (Mw = 33.0, Wako), 3-aminopropyl-trimethoxysilane (3-ATS) (Mw = 197, Aldrich) and poly (allylamine hydrochloride) (PAH) (Mw = ca. 70,000, Aldrich) and counter polyanion used was polyphosphoric acid (PPA) (Aldrich). Protonated amino groups behave as cations. Acid polymers were used for basic gases such as trimethylamine. Acid polymers used were poly(acrylic acid) (PAA), poly(sodium 4-styrene sulfonate) (SPS) and PPA. These structures were shown in Fig. 1. Metal oxide nanoparticles were also used to adsorb toxic gases. Metal oxide nanoparticles used were TiO₂ (Ishihara sangyo, STS-01,

7nm) for basic gases, ZnO (Wako, 20nm) and MnO₂ powder (Wako) for sulfur gases.

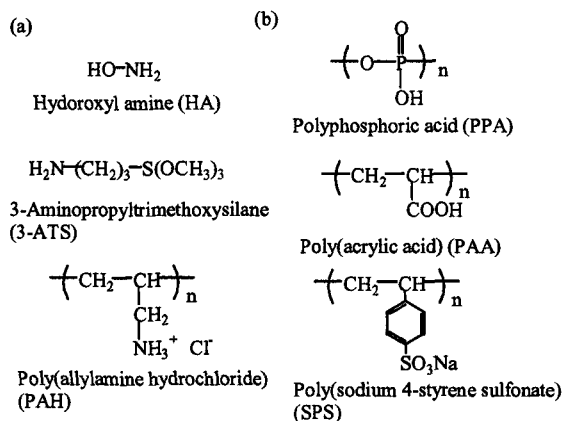


Fig.1 Chemical structure of primary amine compounds (a) and monomer units of acid polyanion (b).

2.2 Methods

Chemical adsorption measurements between primary amine compounds and acetaldehyde gas as carbonyl compounds were carried out by using simple QCM sensor. A cast film on QCM was prepared by dropped the 10mM solution of each amine compound (5.0μl) and dried. Film mass was calculated from the frequency change before and after casted. This QCM exposed for 30 minutes to acetaldehyde gas (30ppm) and film mass that increased by the chemistry adsorption of the acetaldehyde was measured. Just the same time reactivity between acid polymer and trimethylamine was measured.

Alternate assembly film was fabricated using mass-control automatic dipping machine, adsorption was monitored using QCM (AT-cut, 10MHz, Ag-electrode) and it was observed as indicated by mass increase corresponding to frequency shift. In this study 1Hz frequency shift was corresponded to the 1ng mass increase [10,11]. A QCM electrode was immersed in a 1.0wt% KOH solution (H₂O 40% / C₂H₅OH 60%) for 120 sec to obtain a negatively charged surface, rinsed with de-ionized water and dried. The QCM substrate was dipped alternately in 10mM anionic solution and 10mM cationic solution for 300 sec and intermediate rinsing twice for 60 sec each.

Gas removal measurements were carried out using a homemade apparatus. An airtight container (56.0l) was made from acryl resin with fitted up a fun for diffusion. Supporting membranes used were glass fiber and size of membranes was 8×8cm². Because this glass fiber hasn't porosity (real surface area is 1.8m²/g), it used to measure only gas removal performance of only layer-by-layer self-assembly film. Layer-by-layer self-assembly film was fabricated on this film with a same condition, dried at 90°C and fitted up with a fun in the container. Container made fill with toxic

gas and the performance of these filters was evaluated by inspection tubes method.

3. RESULTS AND DISCUSSION

First gas adsorption measurements were considered. Chemical adsorption performance between primary amine compounds and acetaldehyde gas as carbonyl compounds is shown in Fig. 2. Vertical axis explains adsorbed amount of acetaldehyde gas of unit film mass. As for HA, the basification is strong because the nitrogen is covalently bonded with oxygen and also generated imine compound is suitable, HA has a high reactivity with acetaldehyde and fast kinetics in comparison with PAH and 3-ATS. Reaction between HA and aldehyde is expressed following Fig. 3. Reactivity with trimethylamine and acid polymer was measured. It is assumed that PPA adsorb trimethylamine gas the best, because phosphoric acid is a stronger acid and more over molecular weight of PPA is small.

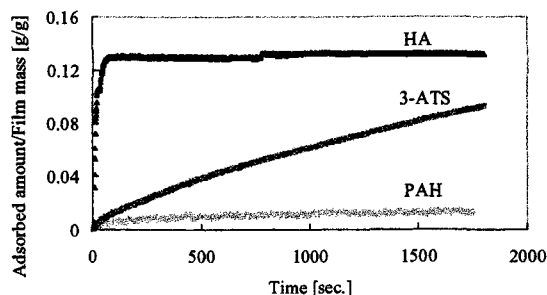


Fig.2 Reaction of primary amine compounds with acetaldehyde gas.

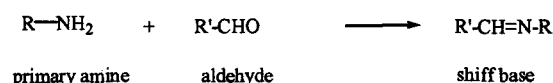


Fig.3 Chemical reaction of aldehyde with primary amine compound.

It was identified by Fourier Transform infrared spectroscopy (FT-IR) whether this reaction will occur between solid phase and vapor phase. PAH and PAA exposed to acetaldehyde gas were measured. From the spectra it can be seen that a band around 1600 cm⁻¹ shifted, which is ascribed to amine groups changed to imine groups and which implies that aldehyde gas adsorbs chemically.

There is a need to fabricate alternately assembled film using small molecules because HA has high reactivity. At the first we examined a dependence on solution concentration for primary amine and PPA self assembled films. Relation between solution concentration and adsorbed amount per one bilayer is shown in Fig. 4. Adsorbed amount increases with concentration until reaching a plateau at PAH (17.0mg/m²), 3-ATS (2.7mg/m²) per one bilayer. Equilibrium adsorbed amount of PAH/PPA is about six times as much as that of 3-ATS/PPA. Desorption in the

aqueous solution of assembled film causes of little adsorption quantity compared with polymer. The film using 3-ATS grew, however, HA self-assembled films couldn't grow because desorption occurred in a solvent.

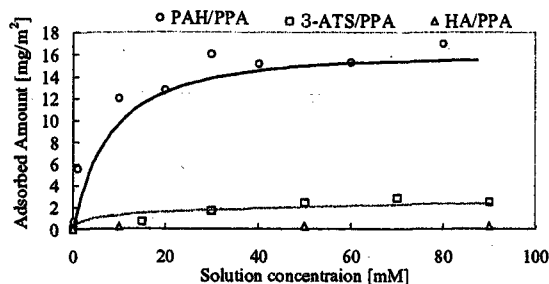


Fig. 4 Adsorbed amount per 1 bilayers as a function of solution concentration. PAH/PPA (circles), 3-ATS/PPA (squares), HA/PPA (triangles).

Therefore we tried to fabricate HA/PPA film by changing the pH value of the solution. Relation between the pH value of HA and adsorbed amount is shown in Fig. 5. It was confirmed that the alternately assembled film grows in the certain particular pH range. Area A and B is expressing the result by the difference of pH value of PPA solution (A: pH = 4.0-5.0, B: pH = 10.0-11.0) and adsorbed amount is the value at the time of 1 bilayer. As shown in Fig. 5, the adsorbed amount increases considerably for HA pHs between 8.0 and 10.0, where HA is a little protonated. Because there is little electric charge quantity of HA, it is considered that adsorption amount increased when it would neutralize the opposite electric charge of the substrate surface.

It was succeeded in producing an alternately assembled film using low molecular weight organic compounds by changing the pH value of the solutions, but adsorbed amount wasn't enough. And we studied on the relation between adsorbed amount of HA/PPA LbL SA film and dielectric constant (ϵ). It is conceivable that the solubility of the complex becomes small and desorption will be controlled, if the polarity of a solution becomes small. We used water ($\epsilon=78.6$, 25°C), ethanol ($\epsilon=24.3$, 25°C) and ethyl acetate ($\epsilon=6.0$, 25°C) as a solvent and the relation between frequency shift and number of cycles were shown in Fig. 6. It was confirmed that frequency change increased as the dielectric constant of the solvent was smaller and adsorbed amount reached about as much as polymer when ethanol and ethylacetate mixed solvent were used. Anion and cation absorb alternately by the electrostatic interaction and grow as a hetero structure and an interface electric double layer model explains the mechanism:

$$\phi = \delta \sigma / \epsilon \quad (1)$$

Where ϕ is surface potential of a solid, σ is density of electric charge, δ is the distance between positive and negative electric charge and ϵ is the dielectric constant of solution. Whether or not oppositely charged molecule adsorbs on a solid surface depends

on the value of ϕ and adsorption is easy to occur, as ϕ is larger. Here it supposes that δ is not change. When ϵ becomes smaller, the dissociation degree of an electrolyte falls off and σ becomes smaller. However ϕ shows the same order as a water system and desorption is suppressed so it is conceivable that it becomes easy to adsorb. There is several report about dye-containing layer-by-layer assembly regarding the alternate assembly using linear polyions and charged small molecules [12-15], however, their small molecules adsorption properties is the first detail physical measurements.

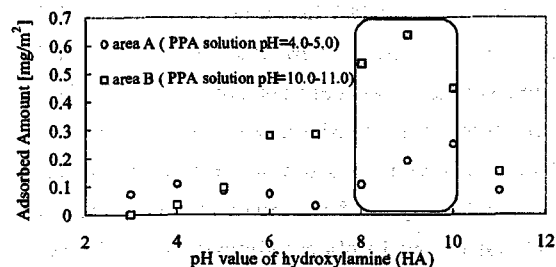


Fig. 5 Adsorbed amount of HA/PPA LbL SA film on QCM as a function of hydroxylamine solution pH. Adsorbed amount is the value at the time of 1 bilayer. PPA pH = 4.0-5.0 (circles), PPA pH = 10.0-11.0 (squares)

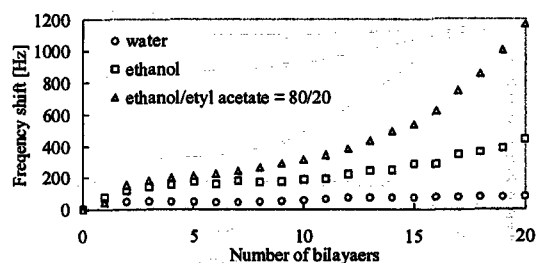


Fig. 6 Influence of the dielectric constant of dissolvent in HA/PPA layer-by-layer self assembled films: water(circles), ethanol(squares) and ethanol/ethyl acetate = 80/20(triangles).

Next we made films using oppositely charged colloidal particles with linear polyions [16]. Alternate adsorption states using metal oxide was measured. Fig. 7 shows the QCM frequency shift of alternate MnO_2 and PAH adsorption. A linear increase in adsorbed amount with number of bilayers has been observed. TiO_2 /PPA and ZnO /PAA self-assembled films could be fabricated similarly.

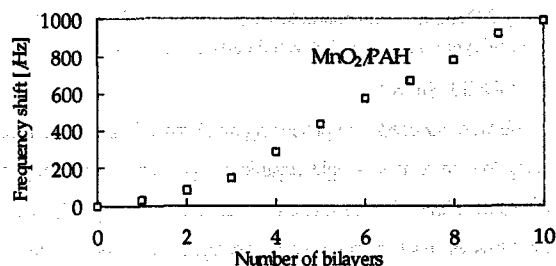


Fig. 7. Frequency shift (- ΔF) of QCM upon metal oxide/polycation assembly.

Gas removal effect using airtight container was carried out. Fig. 8 and Fig. 9 shows deodorization characteristics of formaldehyde and trimethylamine. The horizontal axis expresses progress time

and vertical axis is showing the density of formaldehyde gas. Initial density inside the system was arranged at 4.0 ppm and 60ppm. As the result of gas removal test, removal performance of HA/PPA was higher than that of PAH/PPA. HA/PPA self-assembled film (20 bilayers) fabricated using mixed solvents (ethanol/ethyl acetate = 80/20) was tested similarly. Gas removal performance was improved because adsorbed amount was increased as number of cycles increased. It was confirmed that performance was improved by using alternately assembly of HA/PPA film. Because both TiO_2 and PPA have deodorization capability of trimethylamine, TiO_2 /PPA has higher capability than PAH/PPA film. A deodorization characteristic of TiO_2 /PPA and for trimethylamine gas was better than that of activated carbon. Gas removal test about methylmercaptan was carried out similarly. Initial density inside the system was arranged at 5.0 ppm. Gas removal efficiency (%) after 30 minutes of MnO_2 was 50%, that of ZnO was 30% and that of activated carbon was 75%. Efficiency of the filter using nanoparticles couldn't exceed activated carbon.

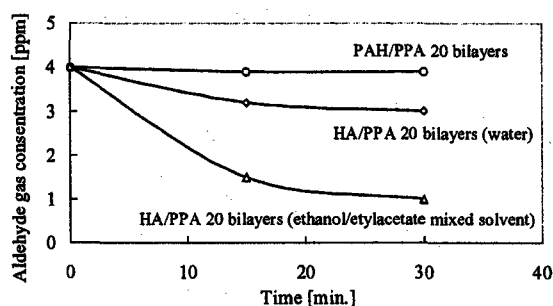


Fig.8 Deodorization characteristics of formaldehyde gas.

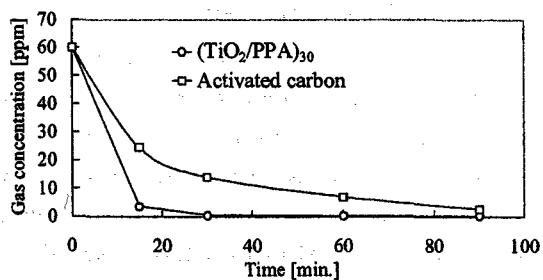


Fig.9 Deodorization characteristics of TMA gas. TiO_2 /PPA 30 bilayers (squares), Activated carbon (circles)

4. CONCLUSION

We were succeeded in producing an alternately assembled film using low molecular weight organic compounds by changing the pH value of the solutions and it was succeeded in the production of the films as much as polymer by changing dielectric constant of dissolvent. From that the possibility of the layer-by-layer self-assembly film production using low molecular weight organic compounds was shown, the improvement extends the technical advantage of layer-by-layer self-assembly considerably and even the contribution to development of the new functional material is

expected. Also it recognized that layer-by-layer self-assembly technique could apply to a filter for deodorization. Now more studies on the fabrication of removing harmful gas are in progress. It has been considered about mixed gas.

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